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DEVELOPMENT OF IMPLANT MATERIALS WITH A GRADIENT POROUS STRUCTURE FOR NEUROSURGERY

B. I. Beletskii,[1] D. Sh. Mastryukova,[1] and E. B. Vlasova[1]

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Biocomposite materials with a gradient pore structure based on a silicate feldspar matrix and hydroxyapatite are analyzed. Porosity and pore size intervals are determined with respect to implants used in neurosurgery, taking into account differences in the process of osteogenesis occurring on different surfaces. In contrast to osteoconductive calcium-phosphate biocomposites with a uniform pore structure, a gradient pore structure provides for a multiple increase in strength of materials.

Calcium-phosphate biological materials have been lately acquiring increasing significance for medicine. They represent an alternative to materials traditionally used in bone surgery and stomatology: metals, polymers, and bone transplants [1, 2]. Inorganic bioactive materials are biologically compatible with live tissue and at the same time have sufficient strength. Preference is given to porous materials whose pore size is sufficient for its colonization with bone cells, which makes these materials osteoconductive. Such materials have perfect compatibility with live tissues.

A disadvantage of these materials under porosity of 50% and more is their low mechanical strength, i.e., in materials with uniform porosity any increase in mechanical strength by decreasing porosity or decreasing the size of pores significantly deteriorates their biological properties.

One of the ways for improving mechanical properties of biocomposite materials and implants based on them is the development of substantiated gradient pore structures for each particular implant. A zone of maximum loading of a bone (88 – 164 MPa) is its cortical layer, whose elasticity modulus is 5 times higher and which is 3 times stronger than spongy bone (up to 15 MPa). This fact was laid in the basis of the development of implants with integral volume variation of porosity and, accordingly, strength [3].

The purpose of our study was to develop composite materials and implants with a porosity gradient to be used in neurosurgery. Existence of a series of composite materials with different levels of density and porosity makes it possible to develop implants reproducing the heterogeneous structure of bone tissues contacting with implants. In developing biomaterial compositions, the intent was to take into account the ratio of the specific surface areas of the matrix and the filler, since a significant difference between the specific surface areas of initial powders and the implant components may cause stresses and, consequently, may originate cracks.

The compositions of materials based on hydroxyapatite (HA) with formula $Ca_{10}(PO_4)_6(OH)_2$ and atomic ratio Ca : P equal to 1.67 and a feldspar matrix of glass NS-2A [4, 5] determining the sintering process, as well as combinations of compositions used to stabilize spinal bones and to substitute for cranial fornix bones are listed in Tables 1 and 2. Glass NS-2A has the following composition (wt.%): 73.0 SiO_2, 11.0 Na_2O, 1.0 MgO, 7.0 CaO, 2.5 B_2O_3, 3.5 Al_2O_3, and 2.0 K_2O.

The optimum sintering schedule for samples with a gradient pore structure is shown in Fig. 1.

The sintering schedule includes the following stages: heating at a rate of 150 – 170 K/h to a maximum temperature of 800°C and an exposure at this temperature for 40 – 45 min. The viscosity of the glass matrix at the sintering temperature is $10^{7.5}$ Pa · sec.

The optimum ratios of the specific surface areas of powders (Tables 1 and 2) were found experimentally and vary from 3 to 7 for fraction of 10 – 50 μm, from 7 to 20 for frac-

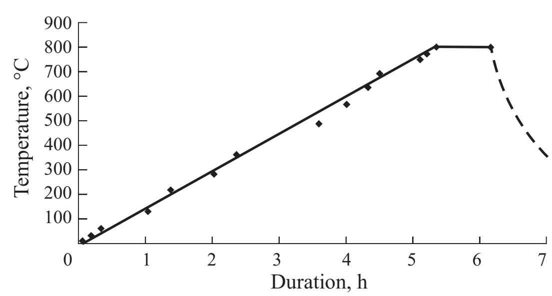

Fig. 1. Optimum sintering conditions for multilayer implants.

[1] D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

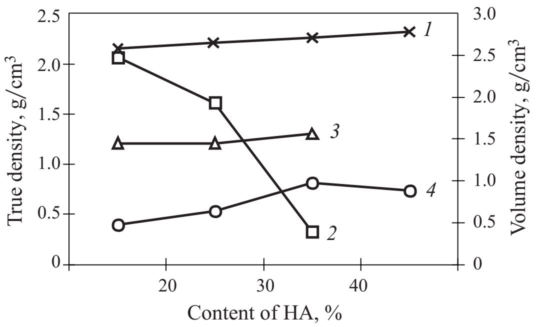

Fig. 2. True density of powders (*1*) and volume density of sintered samples versus a content of HA containing fractions 10 – 50 (*2*), 50 – 200 (*3*), and 200 – 600 μm (*4*).

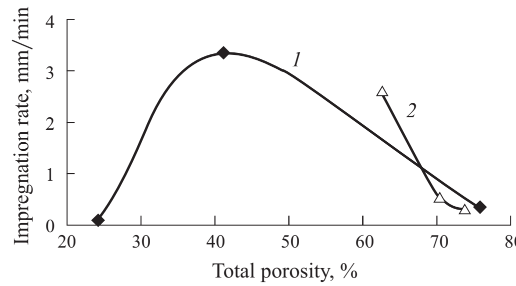

Fig. 3. Dependence of impregnation rate on porosity and pore size of material with a mass content of filler up to 40%: *1* and *2*) rate of impregnation of sintered materials based on filler fractions of 10 – 50 and 200 – 600 μm, respectively.

tion of 50 – 200 μm, and from 30 to 60 μm for fraction of 200 – 600 μm. It can be seen in Fig. 2. that when the filler content in a material with fraction 10 – 50 μm grows above 30%, frothing of the glass matrix takes place, which decreases the volume mass of the material. For the fractions 50 – 200 and 200 – 600 μm the volume mass variation curves are proportional and parallel to the true density variation curve.

In view of medical requirements imposed on porous biocomposites, permeability is one of the key properties (Fig. 3). As porosity and the pore size increase, the rate of impregnation decreases due to a decreasing capillary suction effect. The smaller the pore size, the more intense this effect is. Consequently, in developing materials with gradient porosity, the rate of impregnation should decrease from a compact outer layer toward an inner porous layer.

A non-standard experimental method was used to test the resorption capacity of implant materials. Samples were placed in 0.6-N solution of HCl, which multiply exceeds the concentration of HCl in a human body [6]. The results of the experiments are shown in Fig. 4.

The yield of phosphate ions with a content of HA increasing up to 40% grows in all fractions. A composition based on the fraction 10 – 50 μm exhibited a decrease in the weight loss due to high sealed porosity.

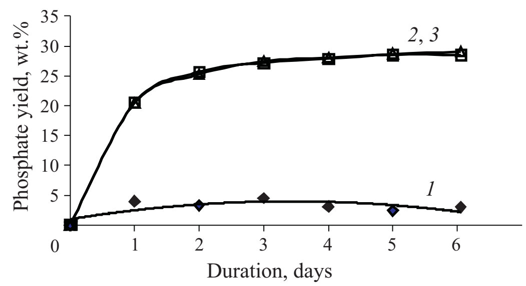

Fig. 4. Resorption capacity of implant material with filler content up to 40%: *1*, *2*, and *3*) the filler fraction sizes 10 – 50, 50 – 200, and 200 – 600 μm, respectively.

The results obtained in electron-microscope analysis (Fig. 5) testify that pore size variation is not monotonic, although theoretically pore sizes should decrease, as the size of the filler fraction decreases.

Samples of fractions 50 – 200 and 200 – 600 μm exhibit an increased pore size due to the growth of the volume of inter-grain voids, and large pore sizes in fraction 10 – 50 μm are due to the frothing of the glass matrix, since a high content of HA in the composition of fine fractions has a substantial effect on the temperature of decomposition of the gas-forming compound $CaCO_3$, which leads to foaming of the glass matrix.

TABLE 1

Sample	Fraction, μm	Component ratio, %	
		NS-2A	HA
1	10 – 50	80	20
2	10 – 50	70	30
3	10 – 50	60	40
3b	50 – 200	80	20
4	50 – 200	70	30
5	50 – 200	65	35
6	50 – 200	60	40
7	200 – 600	80	20
8	200 – 600	70	30
9	200 – 600	60	40
10	200 – 600	50	50
11	200 – 600	45	55

TABLE 2

Type of implant*	Cortical layer**	Spongy layer**	
		I	II
E.3	2	9	8
C.2	9	8	–
D.2	2	9	–
F.2	2	8	–

* E.3) three-layer elliptical spinal implant; C.2) two-layer cylindrical spinal implant; D.2) two-layer cranial fornix implant; F.2) two-layer implant for cranium fornix bone.

** Numbers of powder compositions (Table 1).

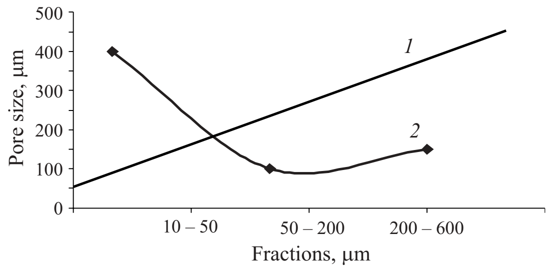

Fig. 5. Dependence of pore size in material on fraction sizes of filler contained in amount of 40%: *1*) theoretical variation of pore sizes depending on the filler fraction sizes; *2*) experimental data.

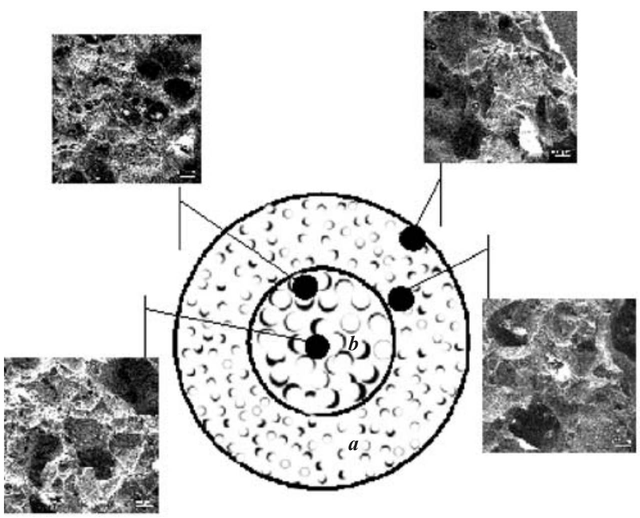

Fig. 6. Electron microscope photos of two-layer cylindrical implant (× 100): *a*) cortical layer, composition 9; *b*) spongy layer, composition 8.

Several compositions were selected for strength testing and tested simultaneously with the standard reference sample: BAK-1000 [6] of fraction 200 – 900 μm with a matrix-to-filler ratio equal to 55 : 45% (Table 3).

A decrease to 20% in the content of the filler containing fraction of 10 – 50 μm (sample 1) produces a 9-times increase in the strength of the material and doubles the volume mass compared to the reference standard. Such compositions are recommended for use in developing implants for stomatology, namely, the crown of a tooth.

After a multilayer materials with gradient porosity was obtained, its microstructure was investigated by electron-microscope analysis (Fig. 6). It can be seen in the photos the pore size changing from a compact cortical layer to a spongy layer.

The materials obtained were sent to the Meditsina and Biotekhnologii Company to implement planting of fibroblast cell cultures. Preliminary results of fibroblast cultivation demonstrated good prospects for using these materials as a substrate for growing cells outside a living body.

The composite material based on glass NS-2A and HA is an alternative to materials based on polymers. Consequently, even partial replacement of polymer materials by inorganic ones in medical practice decreases environmental damage caused by polymer production.

The material specified has a relatively low cost compared with its world analogs. The cost of the Interpore material, for instance is \$150 per cm^3, whereas our material costs \$30 per cm^3.

The following conclusions can be drawn on the basis of estimated and experimental data.

The strength and carrying load of implants depend not only on the sintering schedule, but also on two more parameters: the granulometric composition of the filler and its content in the material, and also the ratio of volumes of the compact and spongy layers in the implant.

Furthermore, it is necessary to take into account the differences in the process of osteogenesis on different surfaces. Modifications of the pore sizes and total porosity of layers of different density produce certain modifications in the formation of bone tissue on the surface and inside the volume of an implant.

Osteogenesis on the cortical layer of the implant proceeds on the surface with formation of periosteum, accordingly the pore size should be below 100 μm, and osteogenesis in the spongy layer proceeds inside the volume, accordingly the pore size should range from 100 to 500 μm for intergrowth of bone tissue cells and subsequent vascularization of calcination.

By varying the matrix-to-filler ratio, the granulometric composition and the total content of filler in the material, and

TABLE 3

Composition	HA fraction, μm	Glass NS-2A : HA, %	Density, kg/m^3	Total porosity, %	Loading surface area, cm^2	Loading, kN	Compressive strength, MPa
			References standard values				
BAK-1000	900 – 200	55 : 45	1000	60	3.8	2.5	6.6
			Experimental data				
8	600 – 200	70 : 30	640	71	9.5	2.4	2.5
9	600 – 200	60 : 40	980	65	6.3	1.4	2.2
6	200 – 50	60 : 40	1300	52	3.8	4.8	13.0
2	50 – 10	70 : 30	1610	41	4.8	3.4	7.0
1	50 – 10	80 : 20	2060	24	3.5	41.0	119.0

the ratio between the volumes of the compact and the spongy layers, one can obtain different pore structures and, accordingly, individual implants with a gradient pore structure and, consequently, significantly increase the mechanical strength of implants and bring their structure as close as possible to the structure of bone tissues contacting with the implant.

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